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(54) Title: AQUEOUS COMPOSITIONS COMPRISING COMPLEXING AGENTS AND USES THEROF

(57) Abstract

The invention relates to aqueous compositions, comprising calcium ions and metal ions selected from the group comprising Cu, Fe, Zn, Ni and Co, and a specific complexing agent and applications for these aqueous compositions.

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AQUEOUS COMPOSITIONS COMPRESING COMPLEXING AGENTS AND USES THEROF

Technical Field

The invention relates to aqueous compositions comprising calcium ions and metal ions selected from the group comprising Cu, Fe, Zn, Ni and Co, and a specific complexing agent.

The invention also relates to the use of a specific complexing agent for selectively complexing selected metal ions, in the presence of calcium ions.

Background to the Invention

In a variety of technical fields the presence of certain metal ions such as heavy metal ions is undesirable because it is known that they can adversely affect the performance of various technical processes. In general, chelating or complexing agents are used to ameliorate this problem.

For example, in pulp, paper or textile bleaching or de-inking, metal ions tend to reduce the efficiency of the bleaching process and also tend to produce colour in the paper (or textile) product, iron ions being the most detrimental to achieving brightness. The bleaching processes are enhanced through the use of chelants or sequesterants that inactivate metal ions. However, a problem can be that these chelants are not bleach stable, in particular when oxidative bleaches are used . The most well-known chelants are aminomethylene carboxylates, such as NTA and EDTA and their salts.

The presence of certain metal ions can be detrimental in other technical fields. For example in dyeing processes, certain dyestuffs are detrimentally affected by various metals, especially alkaline-earth metals or heavy metals such as iron and copper, which

can be accidentally present in the dyeing bath. These metals have the effect of causing agglomeration or flocculation of the dyestuff, modifications of tone and depth of colour, a decrease in the transfer of dye to the textile fibres and a reduction in the fixation of the dyestuff to the fibre. To reduce the negative impact of these metals upon the physical and colouring properties of a dyestuff, complexing agents are used, for example polyphosphate complexing agents, to render ineffective certain metal ions.

In food products, various ingredients are not stable to oxidation and the products can become rancid upon storage. It is known that the oxidation process is catalysed by certain metal ions. Thus, various chelating agents are commonly employed to reduce the catalytic activity of these metal ions and to improve the stability of the ingredients, for example citric acid and ascorbic acid. Metal ions may also adversely affect the performance of yeast.

In other technical fields, the presence of certain metal ions such as heavy metal ions is actually needed and a controlled delivery of metal ions or a control-system to maintain a certain amount of metal ions can be essential to the well-functioning of these applications. For example, in methods of magnetic resonance imaging, delivery of specific metal ions in the human body is needed; in (waste) water treatment, certain metal ions are needed to inhibit algae growth; in methods for electroless plating, metal ions are required to plate metal surfaces; in scale removal processes where not only metal ions have to be removed but also metal oxides can be used to form a coating on the surface, to avoid scale deposition; in agricultural processes to deliver nutrients to the plants; in tanning processes, certain metal ions are required to provide the tanning; In these technical fields, chelating or complexing agents are useful to improve the efficiency of the techniques or processes.

Furthermore, it is known that certain metal ions can cause health or cosmetic problems, for example for example nickel dermatitis and heavy metal poisoning (either by accidental intake of metal ions, or by absorption of iron ions from the cells by failure of

certain body functions); certain enzymatic reactions, which require the presence of certain metal ions, can cause cosmetic or health problems.

Thus, on one hand, it has been a challenge to reduce the negative effects of metal ions and on the other hand, to improve the benefits obtainable by the use of metal ions and therefor, a variety of chelating or complexing agents are developed which can chelate the metal ions.

In the past decades, the main aim has been to develop chelating agents which have an improved binding capacity for heavy metal ions. Well-known chelating agents thereto are, for example, EDTA and DTPA.

The inventors now have found that even those chelating agents which have a very high binding capacity for heavy metal ions, do not always perform very effectively.

The inventors have now found that this can be due to the fact that these chelating agents do not just have a high binding capacity for heavy metal ions, but also for other metal ions which may be present. It has been found that, for example, the presence of calcium ions can reduce the efficiency or effectiveness of certain chelating agents.

The nature of a variety of systems or applications where heavy metal chelating agents are useful, is often such that the presence of calcium ions is unavoidable or even needed. For example, in bleaching, dyeing or tanning processes, large quantities of untreated water may comprise high levels of calcium ions, are used, which can thus affect the heavy metal-chelating capacity of these chelants, when used in these processes; in water reservoirs, in particularly waste-water reservoirs, pools, lakes, irrigation systems etc., high levels of calcium ions are unavoidable; in metal scale removal and metal plating processes, large quantities of calcium ions can be present; in the human body, calcium is present which will have a negative affect on the performance of chelating agents used in treatments; in food products, in particular dairy products, large quantities of calcium are

present, which can reduce the efficiency of commonly used chelating agents, used as preservatives or anti-oxidants, to prevent the food ingredients to oxidise and become rancid. In fermentation processes, it has been found that the presence of calcium ions can be required for the performance of the yeast, whilst the presence of other metal ions is detrimental to the yeast performance, which thus need to be removed.

However, the inventors have now found a solution thereto. They have now found that specific complexing agents are very effective, specific complexing agents for certain metal ions, namely Cu, Fe, Zn, Ni and Co, but not for calcium ions. Thus, these specific agents are very effective complexing agents in technical applications, whereby the presence of calcium is unavoidable or even essential and whereby complexing of specific metal ions is required or whereby delivery of specific, chelated metal ions is required.

Summary of the Invention

The invention provides aqueous composition of the invention, comprising calcium ions, preferably when in use, and one or more metal ions, selected from the group consisting of Cu, Fe, Zn, Ni and Co and comprising a complexing agent, are those whereby - $\log_{10}C_T$ is equal to or greater than the smallest value of A or B, where

$$A \text{ is } -\log_{10}(L_T-M_T) \text{ and } B \text{ is } K_1(1 - K_2\sqrt{I})(1 - K_3.\exp(-K_4.P)),$$

wherein C_T is the total concentration of calcium ions, L_T is the total concentration of complexing agent, M_T is the total concentration of the metal ions, selected from the group consisting of Cu, Fe, Zn, Ni and Co; P is the pH of the composition, I is the ionic strength of the composition, where K1, K2, K3 and K4 are the following constants for the metals ions:

	Cu^{++}	Fe^{+++}	Zn^{++}	Ni^{++}	Co^{++}
K1	11.062	5.754	7.963	13.098	7.642

K2	0.496	0.479	0.619	0.535	0.652
K3	2.479	9385.0	24.202	1.473	32.069
K4	0.227	1.092	0.506	0.126	0.532

All concentrations in the above equation are measured as moles/ litre.

The invention also relates to specific applications for these aqueous compositions, whereby the use of specific complexing agents amounts to the selectively chelating of one or more metal ions, selected from the group comprising Cu, Fe, Zn, Ni and Co, in the presence of calcium ions.

Detailed Description of the Invention

Aqueous Compositions

The aqueous compositions of the invention are defined by a specific pH, the presence of a specific concentration of calcium ions and the presence of specific levels of metal ions, selected from the group Cu, Fe, Zn, Ni and Co (herein referred to as selected metal ions), and a specific level of complexing agents, such that the chelating agent selectively will complex the metal ions.

Said aqueous composition can be obtainable by a process comprising the step of addition of a complexing composition comprising a complexing agent and optionally other compounds, to an aqueous solution, comprising calcium ions.

Depending on the application, the aqueous composition according to the invention may contain the selected metal ions and the calcium ions or may contain the selected metal ions and calcium ions in use

It may be preferred that the selected metal ions in the compositions are chelated or 'complexed' by the complexing agent, thereby preferably forming a complex.

However, it may be preferred that the complexing agent in the compositions is substantially free from these selected metal ions and that in use, the selected metal ions are chelated or 'complexed' by the complexing agent, thereby preferably forming a complex.

When nickel and/ or copper ions are present in the composition, it can be preferred that the composition has a pH of 4 or more. When zinc ions are present in the composition, it can be preferred that the composition has a pH of 7 or more. When iron ions are present in the composition, it can be preferred that the composition has a pH of 9.5 or more.

The aqueous composition is preferably not a composition for use in laundry or dish washing processes or a composition for use in photography or photo-development processes.

It should be understood that for the purpose of the invention and depending on the application of the composition, the calcium ions and optionally the selected metal ions can be present in the compositions to be used in the applications described herein, or the calcium ions and optionally the selected metal ions can be present in the compositions, when in use in the applications.

Furthermore, the levels of incorporation of the complexing and the amounts of calcium ions and selected metal ions will depend on the application of the compositions of the invention. Depending on the application, it may be preferred that the complexing agent and the selected metal ion are present in a stoichiometric amounts, or that one of the components is present in a stoichiometric excess.

Process for Preparation of the Compositions

The aqueous composition can be prepared by a process, comprising the step of addition of a complexing composition, comprising a complexing agent, to an aqueous mixture, comprising calcium ions, whereby the complexing composition comprises one or more of the selected metal ions selected. The complexing agent and the selected metal ions can be added to the complexing composition either separately or as a premix composition, in which they may be complexed.

Alternatively, the aqueous composition can be prepared by a process comprising the step of addition of a complexing composition, comprising a complexing agent, to an aqueous mixture, comprising calcium ions, whereby the aqueous mixture also comprises one or more of the selected metal ions.

Depending on the application of the aqueous composition and the process for preparing the composition, the selected metal ions can have any counterion, preferably sulphate or chorine, and they can be present in the form of alkali metal or ammonium salts.

Complexing Agents.

A highly preferred complexing agent for use in aqueous compositions of the invention is N, N' ethylene diamine disuccinic acid or its salt (EDDS).

It is known that the (S,S) EDDS isomer is more readily biodegradable than the (R,R) isomer. Thus, depending of the application of the aqueous compositions of the invention, it may be desirable to use only one of the isomers of EDDS. It may be preferred that a racemic mixture of the isomers is used in the aqueous compositions, for example because the racemic mixture is less expensive.

The use of EDDS in the compositions of the invention has as an additional benefit that EDDS is very stable, in particular in bleach containing compositions, and that EDDS can

be easily and readily separated from the selected metal ions, when necessary, by formation of cyclic EDDS under specific reaction conditions.

For the purpose of the invention and depending on the application of the aqueous composition, it should be understood that either the complexing agent can be introduced in the composition comprising the selected metal ions, to selectively form a complex with these metal ions, or the complexing agent can comprise one or more of the selected metal ions, prior to introduction into the composition (which can additionally contain one or more of the selected metal ions).

pH Measurement

The pH as used herein can be determined by any known method of calculating or measuring the pH of an aqueous solution.

Ionic Strength Measurement

The ionic strength (I) can be determined by the following equation:

$I = \frac{1}{2} \Sigma c_i z_i^2$,

wherein c is the molecular concentration of the soluble ion (i) and z is the charge of the soluble ion (i).

Additional Ingredients

The aqueous composition of the invention will preferably comprise additional ingredients. The precise nature of the additional ingredients and the levels thereof will depend on the purpose or application of the aqueous composition.

Depending on the application of the compositions of the invention, a preferred additional ingredient can be one or more builders or dispersants. It can be preferred that a crystal growth inhibitor is present, preferably in addition to dispersants.

Suitable examples of water-soluble phosphates, suitable a s crystal growth inhibitors or builders, are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid.

Any builder or dispersant material known in the art can be used. Particularly useful builders or dispersants can be monomeric, oligomeric and polycarboxylate-containing components, polymeric components, borate-containing components and phosphate-containing components and silicate and aluminosilicate-containing components.

Suitable polycarboxylates or polycarboxylic acids can be succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid; citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447; oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates; sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000;

Polymeric components include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 1000-5000 and their copolymers with maleic anhydride, such copolymers having a molecular weight of from 2000 to 100,000, especially 40,000 to 80,000.

The polyamino components are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

Terpolymers containing monomer units selected from maleic acid, acrylic acid, polyaspartic acid and vinyl alcohol, particularly those having an average molecular weight of from 5,000 to 10,000, are also suitable herein.

Other polymeric components suitable for incorporation in the compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose, hydroxypropylmethylcellulose and hydroxyethylcellulose.

Further useful polymeric components are the polyethylene glycols, particularly those of molecular weight 1000-10000, more particularly 2000 to 8000 and most preferably about 4000

Other preferred ingredients are amorphous or crystalline, preferably layered, silicate or aluminisilicate materials or builders. Suitable aluminosilicate zeolites have the unit cell formula $Na_z[(AlO_2)_z(SiO_2)y]$. xH_2O wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate materials are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

Applications

The aqueous compositions are applicable in a variety of applications, where calcium ions are present and selective complexing or binding of the selected metal ions is required. Examples, thereof are bleaching or deinking processes for pulp or paper and bleaching processes for textiles, such as oxidative bleaching and chlorine-based bleaching or in particular reductive bleaching; dyeing processes of pulp, paper and textiles; algea, fungi and bacterial growth stabilisation or inhibition; (electroless) plating or finishing of metal surfaces; removal of metal from waste-water or sludge; metal scale removal; tanning processes such as used in leather manufacturing processes; rubber manufacturing processes; food preparation processes, in particular food preservation processes, in particular for food which is rich in calcium, which is sensitive to oxidation, such as lipid- or protein-containing products; fermentation processes such as used by the production of yoghurt or wine and beer, in particular the wine- or beer-clarification process step thereof; agricultural processes for delivering nutrients to plants; methods for reduction of the enzyme activity of enzymes present on the human skin, including treatment of enzymatic dermatitis; methods for treatment of metal poisoning, such as treatment of metal dermatitis and chelation therapy; and methods for delivering metal ions to the human or animal body or to plants, such as delivering of plant nutrients and methods of Magnetic Resonance Imaging (MRI).

These applications will now be discussed in more detail.

Reductive Bleaching/ De-inking

The process of preparation of the aqueous compositions of the invention, comprising the step of addition of a complexing composition, comprising a complexing agent, to an aqueous solution, comprising calcium ions and one or more of the selected metal ions,

can be part of a reductive bleaching or de-inking process, in particular for cellulosic material such as a cotton, pulp or paper.

Thus, one of the preferred processes wherein the aqueous compositions of the invention can be used are reductive pulp- or paper- or textile-bleaching or de-inking processes.

The reductive bleaching process comprises the step of contacting the pulp, paper or textile with the aqueous composition of the invention, containing the reductive bleaching agent.

The preferred complexing agent of the compositions for use in the bleaching processes is EDDS. The amount of complexing agent employed, may vary in accordance with the nature of the process. Generally, at least 0.001% by weight of the dry pulp of a complexing agent or component is present, more preferably at least 0.01%.

In the reductive bleaching process, large quantities of water are used. Therefore, the calcium ion concentration will generally be determined by the hardness of the used water.

The most preferred reductive bleaching process herein, is a bleaching process for bleaching (deinked) pulp, which uses reductive bleaching agent containing a reducing agent and a bleaching agent , preferably a sulfite or dithionite-based agent. The dithionite ion ($S_2 0_4^{2-}$), thereby provided, is then the active bleaching species. Preferably, the reducing agent more electronegative than the sulfite ion, in a medium initially having a pH ranging from 6 to 12. The reducing agent that is more electronegative than the sulfite ion, hereinafter designated the "reducing agent" is preferably selected from among thiourea dioxide or formamidine sulfinic acid, sodium borohydride and sodium hydrosulfite.

Dithionite is typically provided to the bleaching process in one of three manners: A) a dithionite-based product in dry form may be dissolved and added to the composiitons of the invention and then to a the pulp slurry or textile, B) commercial dithionite solutions products (which have limited storage stabilities) can be added to the compositions of the invention and then to the pulp slurry or textile, or C) dithionite may be generated on-site from sodium borohydride, sodium hydroxide and an available S^{4+} species, such as SO_2, waste HSO^{3-} or HSO^{3-}/SO_2 solution . The chemistry and cycle of an on-site dithionite generation is described, for example, in "Hydrosulfite Bleaching" by R. Barton, C. Tredway, M.Elles & E. Sulivan, Pulp and Paper Manufacture, 3rd Edition, Volume 2, Mechanical Pulping, R.A. Leask (Ed.) Tappi/CPPA Joint Textbook Committee of the Paper Industry (1987).

Suitable alkali metal hydrosulfites include sodium hydrosulfite, potassium hydrosulfite, lithium hydrosulfite, and mixtures thereof. Highly preferred can be zinc derived sodium dithionites, as described in US patent 3,985,674. While available in the anhydrous form, alkali metal hydrosulfites (dithionites) are advantageously used in a solution. Sodium hydrosulfite bleach solutions are produced by various processes, but they commonly involve the reduction of sodium bisulfite solutions, preferably at pH levels around 6.

The amount of reducing agent employed may vary in accordance with the nature of the process. For example, in the case of thiourea dioxide or dithionite, the amount ranges from 0.1% to 5% by weight of the pulp or textile in the dry state. Sodium borohydride is used in proportions of approximately 0.01% to 0.5% % by weight of the pulp or textile in the dry state, typically ranging from 0.05% to 0.25%.

The amount of sulfite-bleaching agent employed is preferably greater than 0.1% by weight of the pulp or textile in the dry state . For example, in the process herein, at least 0.25 and preferably 0.5% to 1.5% by weight of the dry pulp or textile, of sodium dithionite is used.

The compositions used in the bleaching-processes in accord with the invention, preferably comprise a bleaching antioxidant, preferably selected from the group

consisting of ascorbic acid and palmitoyl ascorbate, is brighter than pulp bleached with dithionite blends only or peroxide only. These antioxidants can be effectively added to the process before the bleaching agent is added to the pulp or textile or simultaneously with the bleaching agent bleached.

The reducing agent is conveniently employed in the form of an aqueous solution thereof, for example a solution of 12% by weight of sodium borohydride marketed under the trademark BOROL.RTM. by the Ventron Corporation.

A typical composition in accord of the invention, used in the bleaching process of the invention, comprises from 1% to 3.6% EDDS sodium salt 6% to 15% NaBH 4, 15% to 35% NaOH., and 1.5% to 7% sodium dithionite.

The use of the compositions of the invention leads to a very effective or efficient bleaching, an reduced fabric or paper damage, and a reduced dingy or yellow appearance of the fabric or paper

Oxidative Bleaching/ De-inking

The process of preparation of the aqueous compositions of the invention, comprising the step of addition of a complexing composition, comprising a complexing agent, to an aqueous solution, comprising calcium ions and one or more of the selected metal ions, can be part of oxidative bleaching or de-inking process for cellulosic material such as a cotton, pulp or paper.

Thus, the aqueous compositions of the invention can be used in an oxidative pulp- or paper- or textile-bleaching or de-inking process, which preferably comprises the step of contacting the pulp, paper or textile with the aqueous composition of the invention, containing the oxidative bleaching agent.

The preferred oxidative bleaching agent contains a peroxide source, such hydrogen peroxide. Inorganic perhydrate salts are a preferred source of hydrogen peroxide, which

are normally used in the bleaching process, in the form of the alkali metal, preferably sodium salt at a level of from 0.05% to 20% by weight, more preferably from 1% to 15% by weight and most preferably from 2% to 8% by weight of the pulp, paper or textile.

Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate, preferably potassium peroxymonopersulfate, and persilicate salt. Sodium perborate can be in the form of the monohydrate of nominal formula $NaBO_2H_2O_2$ or the tetrahydrate $NaBO_2H_2O_2.3H_2O$. Sodium percarbonate has a formula corresponding to $2Na_2CO_3.3H_2O_2$, and is available commercially as a crystalline solid.

In the bleaching process, large quantities of water are used. Therefore, the calcium ion concentration will generally be determined by the hardness of the used water.

The preferred complexing agent of the compositions for use in the bleaching processes is EDDS, which has been found to be a very specific and effective complexing agent in the presence of calcium. The amount of complexing agent employed, may vary in accordance with the nature of the process. Generally, at least 0.001% by weight of the dry pulp of a complexing agent or component is present, more preferably at least 0.01%.

An additional advantage of the use of EDDS as complexing agent in an oxidative bleaching process herein, is that EDDS is very stable in the presence of oxygen bleach.

The process can comprise the step of addition of the paper, pulp or textile to a solution containing a alkaline buffer (e.g. NaOH) and sodium silicate, whereto the bleach and the complexing agent are added. It can be preferred however, to add a acidity source (e.g. H_2SO_4 or H_2SO_3) to the paper, pulp or textile, prior to addition of the bleach and the complexing agent.

Additionally, chlorine-base bleach can be present.

Chlorine-Based Bleaching/ De-inking

The process of preparation of the aqueous compositions of the invention, comprising the step of addition of a complexing composition, comprising a complexing agent, to an aqueous solution, comprising calcium ions and one or more of the selected metal ions, can be part of chlorine-based bleaching or de-inking process for cellulosic material such as a cotton, pulp or paper.

Thus, the aqueous compositions of the invention can be used in a chlorine-based pulp- or paper- or textile-bleaching or de-inking process, which preferably comprises the step of contacting the pulp, paper or textile with the aqueous composition of the invention, containing the chlorine-based bleaching agent.

Depending on the application, the chlorine-based bleaching agent is typically present at a level of from 0.05% to 20% by weight, more preferably from 1% to 15% by weight and most preferably from 2% to 8% by weight of the pulp, paper or textile.

In the bleaching process, large quantities of water are used. Therefore, the calcium ion concentration will generally be determined by the hardness of the used water.

The preferred complexing agent of the compositions for use in the bleaching processes is EDDS, which has been found to be a very specific and effective complexing agent in the presence of calcium. The amount of complexing agent employed, may vary in accordance with the nature of the process. Generally, at least 0.001% by weight of the dry pulp of a complexing agent or component is present, more preferably at least 0.01%.

The chlorine-based bleach is such that a hypochlorite species is formed in aqueous solution. The hypochlorite ion is chemically represented by the formula OCl^-.

Those bleaching agents which yield a hypochlorite species in aqueous solution include alkali metal and alkaline earth metal hypochlorites, hyposchlorite addition products, chloramines, chlorimines, chloramides, and chlorimides. Specific examples of compounds of this type include sodium hypochlorite, potassium hypochlorite, monobasic calcium hypochlorite, dibasic magnesium hypochlorite, chlorinated trisodium phosphate dodecahydrate, potassium dichloroisocyanurate, sodium dichloroisocyanurate sodium dichloroisocyanurate dihydrate, trichlorocyanuric acid, 1,3-dichloro-5,5-dimethylhydantoin, N-chlorosulfamide, Chloramine T, Dichloramine T, chloramine B and Dichloramine B. A preferred bleaching agent for use herein of the instant invention is sodium hypochlorite, potassium hypochlorite, or a mixture thereof.. A preferred chlorine-based bleach can be Triclosan (trade name).

Most of the above-described hypochlorite-yielding bleaching agents are available in solid or concentrated form and are dissolved in water during preparation of the compositions of the invention. Some of the above materials are available as aqueous solutions and are as such added to the process or the aqueous composition of the invention.

Electroless Plating/ Corrosion Protection

The processes of preparation of the aqueous compositions of the invention can be part of a process for electroless plating.

Thus, the aqueous solutions of the invention can also be used in a process for electroless plating of metal surfaces, whereby calcium ions are present.

In general, the process comprises contacting a metal surface with the aqueous solution. Thus, a preferred process comprises the step of placing a metal surface in an aqueous solution of the invention, preferably comprising, as (one of) the selected metal ions, copper or zinc ions.

In a preferred process, , for example copper ions are reduced at the metal surface/solution interface and then deposited on the metal surface. In this preferred process, the used aqueous solution in accord with the invention, comprises a complexing agent which selectively binds those metal ions which need to be reduced for plating. This can be useful to prevent or reduce metal hydroxide precipitates forming and to buffer the amount of metal ions available for reduction, thus obtaining an effective and even plating. Any reduction method or reduction agent can be used in the process of the invention to reduce the metal ions.

In another preferred embodiment, the metal ions, preferably in the form of a metal salt, such as zinc salt, is present in the composition of the invention, and the complexing agent selectively forms a complex with the metal ion, which is deposited on the surface to thus from a thin 'film', which can protect the surface from corrosion.

Typical electroless plating solutions are described in Industrial Electro-Chemistry (2nd Edition, 1990, published by Chapman Hall, in particular pages 426-429 thereof) by Derek Pletcher and Frank Walsh.

The complexing agent is preferably EDDS, preferably present in a ratio to the metal ion to be reduced or to be deposited on the surface, of from 5:1 to 1:50.

It can be preferred that additional stabilizers are present to stabilise the sulfite-based bleach, such as additional complexing agents or builders.

Metal Scale Removal

The process of preparation of the aqueous compositions of the invention, comprising the step of addition of a complexing composition, comprising a complexing agent, to an aqueous solution, comprising calcium ions and one or more of the selected metal ions, can be part of a process for removal of scale containing one or more of the selected metal ions.

Thus, the aqueous solutions of the invention can also be used in a process for removal of metal scale, whereby (high quantities of) calcium ions are present, preferably from metal surfaces.

The metal scale removal process comprises the step of contacting the scale with an aqueous solution of the invention.

In a preferred process, the composition of the invention can be useful for removal of metal scale, which comprises one or more of the selected metal ions, from any (metal) surface which can be in contact with calcium ions, such as calcium ions contained in water.

For example, the process can be used for cleaning of industrial cooling systems or heating systems, such as boilers, which are of metallic nature, in particular of iron or steel nature, and which are in contact with calcium ions of the water-hardness, and which can rapidly form iron oxide deposits on the heat transfer surface. The formation of these deposits reduce the heat transfer efficiency. Therefore, the cleaning process of the invention can be useful to improve the efficiency of the cooling system

Most preferably the metal deposits to be removed or the metal surfaces to be cleaned are iron-, zinc-, aluminium- or copper-containing compounds, preferably slat or oxides of these metals. The preferred complexing agent is EDDS, as described herein.

It can be highly preferred that the compositions of the invention comprise a metal oxide, preferably zinc oxide, which can deposit onto the (metal) surfaces to prevent future scale formation, directly on these surface. It has been found that the complexing agent of the compositions can be useful to effectively deposit the metal oxide, preferably zinc oxide, onto the surface.

The precise amount of composition used in the process will depend on the nature of the process. Typically, the process requires the complexing agent to be present in an amount

of from at least 100 ppm, but more preferably from 0.001% to about 10%, preferably from about 0.01% to about 5% by weight of the composition.

It can be preferred that the aqueous composition of the invention, used in the metal-cleaning process, has a pH of at least 4, preferably of about 7 to 10.

The duration of the process, being the contact time of the aqueous solution with the metal surface is preferably from at least 30 seconds or more, but more preferably at least 10 minutes.

The aqueous composition of the present invention, used in the metal scale removal process, can contain additional builders or dispersants, as described herein, to remove additional or remaining deposits form the (metal) surfaces. Other additional ingredeints of the compositions can be oxygen scavengers.

Depending on the nature of the cleaning-process, the aqueous composition can comprise an oxidising agent, which is capable of oxidising the metal ions to be removed, to thus facilitate the removal of the metal deposits in the oxidised form.
Typical oxidising agents which can be effectively employed include, but are not limited to, the alkali metal bromates, the alkali metal peroxides (the alkali metal perborates, potassium permanganate), hydrogen peroxide, air, oxygen, ozone, alkali metal and ammonium nitrites and mixtures thereof.

Fermentation Processes

The process of preparation of the aqueous compositions of the invention, comprising the step of addition of a complexing composition, comprising a complexing agent, to an aqueous solution, comprising calcium ions and one or more of the selected metal ions, can be part of a fermentation process.

The aqueous composition of the invention can be used in fermentation processes, to improve the fermenting by yeast.

Namely, the presence of metal ions, such as one or more of the selected metal ions selected, can be detrimental to the performance of the yeast. As discussed above, it has been found that the presence of calcium ions can be essential for the performance of the yeast but that not all metal ions need to be removed from the yeast or yeast solution and that a selective complexing of the certain metal ions, in particular iron and copper, is required. This can be achieved with the compositions of the invention, which contain the specific selective complexing agents, which thus can prevent or reduce the detrimental effect of these metal ions on the yeast performance.

The fermentation process comprises the step of mixing the aqueous composition of the invention with a composition, comprising fermentable substances and yeast.

Preferred fermentation processes are processes for preparation of dairy products, in particular yoghurt, and alcoholic beverages, such as wine and beer.

It has been found that the use of the compositions of the invention, comprising the complexing agent, result in a reduced sensitivity of the wine or beer against discolouring, effect of temperature changesand exposure to air, resulting in an improved taste and colour of the wine.

In a preferred fermentation process for alcoholic beverages, the mixing step of the aqueous composition and the composition, comprising fermentable substances and yeast, takes place at the moment the yeast is added to the fermentable substances, e.g. the cooled wort, in the proper amount.

After the first 24 hours the fermentation is established and proceeds at an accelerated rate. The temperature of the fermenting wort increases and must thus be controlled to maintain yeast viability. Once the yeast has utilised the fermentable substances in the wort (usually after 7 to 10 days), the temperature is reduced and the yeast begins to settle. The yeast is precipitated and removed from the process mixture and then the complexing

agent and the metal ions can be removed from the process mixture, thereby clarifying the mixture.

An additional ingredient for use in the fermentation process, in particular for wine, can be an anti-oxidant or perservarive, such as ascorbic acid.

Furthermore, in fermentation processes for alcoholic beverages, the use of these complexing agents has as an additional benefit that the clarification of the beverages is improved by an improved removal of the metal-fines.

Food Preparation Processes

The process of preparation of the aqueous compositions of the invention, comprising the step of addition of a complexing composition, comprising a complexing agent, to an aqueous solution, comprising calcium ions and one or more of the selected metal ions, can be part of a food preparation process, in particularly of a food preservation process. Hereby, the complexing agent can serve as a anti-oxidant.

The aqueous composition of the invention is particularly useful in processes for preparation of lipid- or protein-containing products, such as oils, fats, meat and fish and egg-containing products. In particular, the composition is useful in processes for preparation of dairy products, which contain high levels of calcium.

In particularly suitable herein, is EDDS which has been found to be a very efficient, selective complexing agent in the presence of calcium, acting as a anti-oxidant or preservative, inhibiting free-radical formation and thereby preventing or reducing the oxidation of oxidation sensitive ingredients, e.g. reducing or preventing rancidity of the food product, thus improving the taste and appearance of the product.

The selected metal ions present in the process are in particularly copper, cobalt or iron.

The precise amount of composition used in the process will depend on the nature of the process.

Additionally, the composition may comprises other commonly employed food-preservatives or antioxidants, such as ascorbic acid and citric acid or their salts; tocopherol; phosphates, nitrates.

Tanning Processes

The process for preparation of the aqueous composition, comprising the step of addition of a complexing composition, comprising a complexing agent, to an aqueous solution, comprising calcium ions, can be part of a tanning process.

Thus, the aqueous composition of the invention can be used in tanning processes, in particular in processes for tanning of leather, or for artificial-tanning or self-tanning of the human skin.

The process can comprise any additional steps, commonly used in tanning processes and for example described in patent application EP245205.

The processes for tanning of leather can be tanning of (un-) treated, (unhaired) hides, or post-tanning or re-tanning of leather and comprises the step of contacting the leather or hides with the aqueous compositions of the invention.

In the tanning processes, one or more of the selected metal ions as described herein, are present to provide the tanning. The complexing agent of the aqueous compositions of the invention, is used in the tanning processes to selectively complex these metal ions and thereby to improve the tanning efficiency, thus permitting a reduction in the amount of tanning agent and metal ions required for the tanning of the leather, hides or skin.

Preferred metal ions used in tanning processes are zinc, chromium and iron or mixture thereof. In the process herein, these metal ions can be introduced in the aqueous

composition in the form of their salts, preferably sulfate, chloride or oxychloride salts, or can be (partially)comprised in the complexing agent. It can be preferred that an additional complexing agent and a chromium ion are present in the aqueous solutions of the invention, when used in such a tanning process.

It has been found that the compositions of the invention can improve the tanning process and that reduced levels of metal ions are required in the process, which has as an additional benefit that the amount of metal ions which is delivered to the environment, can be reduced.

The preferred complexing agent comprised in the compositions used in the tanning processes is EDDS in its salt or acid form.

Any tanning agent can be comprised in the aqueous compositions of the invention, when used in these processes. Preferably, the aqueous compositions of the invention, when used in the tanning process for tanning leather, comprises (a solution of) mineral tanning salts and/or synthetic tanning agents. This agent can comprise a salt of a synthetic, anionic aromatic tanning agent or its (anionic) precursor. Preferred can be a salt of sulphite or thiosulphite, a salt of a condensation-product of sulphonated phenol- or cresol and formaldehyde; a salt of a naphthalene sulphonic acid-formaldehyde condensation product; a salt of a formaldehyde condensation product of 4,4'-dihydroxydiphenylsulphonates with (hydroxy) arylsulphonic acids

The hides can be contacted with the tanning agent simultaneously with or after the aqueous composition is added to the hides.

Depending on the tanning agent and the metal ion used in the process, the aqueous solution can be acidified or alkalised prior to contacting the hides. When firstly a mineral tanning salt is added to the process, alkalising can be required preferably done by adding Na2SO3. When then secondly a synthetic tanning agent is used, the hides are

preferably neutralised before addition of this synthetic tanning agent to the composition of the process.

The amount of complexing agent and metal ions comprised in the aqueous compositions of the invention, will depend on the nature of the tanning processes. Typical amount of metal ions is from 0.005% to 5.0% by weight of the leather or hides to be tanned; and typical amount of complexing agents can be from 0.05% to 1.8% by weight of the leather or hides to be tanned.

Other additional components can be primary, secondary or tertiary amines, such as alkyl and alkenol amines.

When the tanning process is for re-tanning of leather, the process comprises the step of contacting the leather with the aqueous composition of the invention, which preferably comprises condensation products of sulphonated naphthalene with HCHO, and a neutralising agent, such as an amine compound.

The process can comprise the steps of contacting the hides with the aqueous solution of the invention and than storage of the hides and the composition. The aqueous composition can comprise tanning agents, but the compositions and the hides can also be stored prior to addition of the tanning agent.

Hereby, an additional benefit or advantage can be that the complexing agents comprised in the aqueous compositions can provide preservation of the hides or leather upon storage.

It can also be beneficial that the (part of) the complexing agent and optionally (part of) the selected metal ions are not removed from the treated leather during the process, because they have been found to prevent tanning-stain formation of the leather during use.

In processes of artificial-tanning or self-tanning of the human skin, the aqueous composition of the invention comprises the step of contacting the human skin with the aqueous composition.

It has been found that, when used in processes for self-tanning, the compositions of the invention are very effective in preventing skin damage.

The aqueous composition for use in artificial-tanning processes, can be in the form of a cosmetic cream, lotion, gel, or foam, and preferably in the form of an oil-in-water emulsion.

These compositions can comprise any additional ingredient commonly used in cosmetic compositions. Preferably, it comprises an additional sunscreen. Other preferred additional ingredients can be cetyl alcohol, stearyl alcohal, benzoate, octyl palmitate, dimethicone, polysorbate, glyceryl stearate, polyethylene glycol stearate, methyl glucose ether distearate, plant extracts, vitamins, Mg Al silicate, xanthan gum, glycerin, metabisulfite.

Dyeing Processes

The process of preparation of the aqueous compositions of the invention, comprising the step of addition of a complexing composition, comprising a complexing agent, to an aqueous solution, comprising calcium ions and one or more of the selected metal ions, can be part of a dyeing process.

Thus, the aqueous compositions of the invention can be used in dyeing processes, such as processes for dyeing of fabrics or textiles. In these processes, the complexing agents comprised in the composition can eliminate or reduce the negative impact of certain metal ions on the dyeing efficiency of the process. These metal ions, such as copper,

nickel, cobalt, chromium can be present in or on the fabric or can be present in the dying solution.

The dyeing process comprises the step of contacting the fabric with the aqueous composition. The aqueous composition can mixed with the dyeing solution or the dyestuff, prior to contacting the fabric. Alternatively, the fabric can be contacted with the composition, prior to addition of the dyeing solution or dyestuff.

The amount of composition or complexing agent therein will depend on the process conditions and the type of fabric which is to be dyed. In the dyeing process according to this invention, even small amounts of the compositions can be sufficient to obtain the benefits. In general, when the process comprises the step of mixing of the aqueous composition with the dyeing solution or dyestuff, around 0.005-5 g/ litre solution is required. The process can preferably be performed at about 10-200°C.

Examples of suitable process conditions are described in, for example, US patents 4,619,663; 3,539,445 and 4,339,236 which are incorporated herein by reference in their entireties.

Preferred dyes or dyestuffs can be diazo dyes, sulfide dyes, in particular,red disperse dye colour index 92, blue direct colour index 86, red reactive dye colour index 7, orange dye colour index 63, blue direct dye colour index 81, black direct dye colour index 71, green direct dye colour index 34, blue direct dye colour index 93, violet dye colour index 47.

A preferred complexing agent used in the compositions for use in the dyeing processes, is EDDS in the form of its acid or salt.

Optional further ingredients for use in the dyeing processes, can be further antifoams, dispersants, builders, wetting agents, binders and/or a dust inhibitors.

It has been found that the use of the compositions of the invention results in an more efficient, rapid and levelness dyeing, whereby the dye is more uniform applied to the fabric or textile.

Treatment of Metal Poisoning

The aqueous compositions of the invention can be useful in or as compositions for treatment of metal poisoning. Thus, in accord with the invention, the complexing agents described herein, can be used for preparation of aqueous compositions for treatment of metal poisoning.

The metal poisoning of a human being or animal can be due to intake of metal ions from on external source, for example contaminated food or water, occupational exposure to metals, or it can be due to diseases which adversely affect the metal balance of the body, such as iron-loading. In particular, metal poisoning due to iron can be effectively treated with the compositions of the invention.

The complexing agents and the compositions comprising the agents are found to be highly selective for those metal ions, causing the poisoning, such as iron, in the presence of calcium ions, which are commonly present in the body in high quantities. Thus, it has been found that only very small amount of the compositions or complexing agents are required to obtain a very effective complexing or chelating of the metal ions causing the metal poisoning in the human body, and thus a very effective treatment.

The calcium ions and the selected metal ions can be present in the composition to be used, but are preferably present in the composition when in use.

The level of complexing agent used for preparation of the composition will depend on various factors, such as severity of the poisoning, the body weight of the patient and the method of treatment; if the treatment involves giving the composition be infusion over several hours, the level of complexing agent will generally be around 0.5-2 grams per 24 hours for children and 1-4 grams per 24 hours for adults.

The treatment of the patients can involve any steps which commonly can be used for administering medication, such as administering the composition of the invention by infusion or orally.

Depending on the method of treatment, the composition can comprise additional ingredients, as known in the art, such as carrier material, oil-in-water suspensions, additional vitamins such as vitamin C.

Polymerisation Processes

The process of preparation of the aqueous compositions of the invention, comprising the step of addition of a complexing composition, comprising a complexing agent, to an aqueous solution, comprising calcium ions and one or more of the selected metal ions, can be part of a polymerisation process.

Thus, the aqueous composition can be useful in polymerisation processes. The compositions have been found to improve the efficiency of the polymerisation process by catalysing the reaction and / or by stabilising the polymeric materials against hydrolysis.

For example, in a process for polymerisation of urethane, the hydrolytic stability of the formed polyurethanes is improved by use of the compositions of the invention.

For example in reduction processes for polymerisation of rubber the aqueous compositions of the invention are useful as redox catalyst or in the preparation step of the for redox catalysts.

Pesticidal or herbicidal or compositions: fungi, algae and plant growth inhibition, reduction or stabilisation compositions.

The process of preparation of the aqueous compositions of the invention, comprising the step of addition of a complexing composition, comprising a complexing agent and preferably one or more of the selected metal ions, to an aqueous solution, comprising

calcium ions, can be part of a process for inhibition, reduction or stabilisation of fungi, algae and/ or plant growth.

Furthermore, the complexing agents as defined herein, preferably EDDS, can be used for preparation of aqueous compositions, according to the invention, which are useful as herbicidal or fungicidal or algaecidal compositions for stabilisation, inhibition or reduction of algae, fungi and /or plant growth.

The calcium ions can be comprised in the composition to be used or can be present in the composition when in use.

The compositions, when used for preventing or inhibiting the growth of micro-organisms such as fungi, (aquatic) plants, algae, can be used in any application where such prevention or inhibition is required, such as in ponds, lakes, swimming pools and also be used for protecting e.g. wood, buildings, walls, paths, paint, adhesives, glue, paper, textiles, leather, plastics, cardboard, lubricants, cosmetics, food, caulking, feed and industrial cooling water.

Preferred metal ions are zinc ions, cobalt ions and in particular copper ions; a preferred complexing agent is EDDS, as described herein.

The aqueous composition can be obtainable by a process comprising the step of addition of a complex of a complexing agent and one or more of the selected metal ions, to an aqueous solution, comprising calcium ions.

Alternatively, the aqueous composition can be obtainable by a process comprising the step of addition of a complexing agent to a aqueous solution comprising one or of the selected metal ions, and calcium ions.

Preferably, a complex of the complexing agent and the selected metal ion is formed and subsequently added to the aqueous solution. To form such a complex, the complexing

agent is generally used in a weight ratio of 0.20 to 5 parts to one part of (the salt of) the selected metal ion(s).

The proportions of the complexing agents and the selected metal ions can vary within wide limits, depending on the application of the compositions. Generally, the (complexes of the) complexing agent and the selected metal ions will be used at a level of 1% to 90% by weight of the compositions, whereby 30% to 70% are preferred.

The composition can be applied in concentrated form or it can be diluted generally in the ratio of about 5 parts to 100 parts of water and the diluted solution is then applied, as described above.

A preferred copper-EDDS complex for use in the compositions can be prepared by mixing an aqueous solution containing a salt of EDDS and an aqueous solution containing copper sulphate, preferably a copper sulphate-triethanolamine complex.

Any additional ingredients useful in bactericide or herbicide compositions can be present in the compositions. Preferred additional ingredients can then be chlorides, such as calcium chlorides, chlorine -based bleaches, a buffer solution in water/ alcohol or alcohol esters, for example: NaCl, NH4Cl, Na2SO4 and cetyl/oleic alcohol mono-ester in water.

Tertiary amines or (polymeric) quaternary ammonium salts can also be useful additional ingredients in the compositions of the invention when used for preventing or inhibiting the growth of fungi, algae or plants growth. A preferred compound can be dimethylbenzylammonium chloride.

Also other bactericidal or pesticidal or fungicidal agents can be present in the composition of the invention.

Other ingredients can be benzoyl acids or derivatives thereof, benzene or benzene derivatives, such as chlorobenzene, nitrilobenzene and benzene imidazol, and cyano-derivatives.

The compositions of the invention can be applied directly to the subject or environment or solution which needs protection from the of algae, plant, fungi growth or the elimination or reduction of the algae, plant, fungi growth, the compositions can be incorporated into another media, for example paints, agricultural sprays, and then applied to the subject or environment or solution which needs protection from the of algae, plant, fungi growth or the elimination or reduction of the algae, plant, fungi growth.

Plant Nutrients

The process of preparation of the aqueous compositions of the invention, comprising the step of addition of a complexing composition, comprising a complexing agent and one or more of the selected metal ions, to an aqueous solution, comprising calcium ions, can be part of a process for delivering plant nutrients to plants, in particular to improving the growth of the plants and to improve the development of chlorophylls in the plants.

Furthermore, the complexing agents as defined herein, preferably EDDS, can be used for preparation of aqueous compositions, according to the invention, which are useful as plant nutrient compositions for improvement of the plant growth.

A preferred metal ion present in the plant nutrient compositions can be iron.

The compositions can comprise additional ingredients, commonly employed in plant nutrient compositions.

The compositions can be applied to the plants by any known method, for example by foliar application or by spraying-on the composition on the roots of the plants.

Enzyme Activity Reduction

The aqueous compositions of the invention can be useful in or as compositions for reduction of the enzyme activity of enzymes, which require a metallic cofactor containing iron, copper, cobalt, zinc or nickel metal ions.

In a preferred aspect, the enzymes are in contact with the human or animal body.

The enzymes can be enzymes from bacteria's, fungi, algae, or from humans or animals.

In a highly preferred aspect of the invention, the compositions are used for reduction of the enzyme activity of enzymes present in the exudates, in particular esterase enzymes, including lipase enzymes.

Thus, in accord with the invention, the complexing agents described herein, can be used for preparation of aqueous compositions for reduction of the enzyme activity of these enzymes, in contact with the human or animal body or skin. The compositions comprise in use calcium ions, which can be present in the compositions and/ or in or on the human or animal body, and they comprise in use the selected metal ions.

In particular esterase enzymes, including lipase enzymes, are very effectively inhibited or inactivated by the compositions of the invention.

In a highly preferred aspect, the compositions are used for treatment of enzymatic dermatitis and/ or treatment of malodour of the body.

In preferred embodiments of the invention, the compositions comprising the complexing agents are useful for the treatment of enzymatic dermatitis or the treatment of formation of a malodour of the body, caused by enzymes, in particular for reduction of the enzyme activity of lipase enzymes.

The preferred complexing agent herein, is EDDS, as described above.

By treatment is meant herein an improvement of the affected condition of the human or animal body, caused by the enzyme activity. Thus includes in one preferred aspect of the invention, the reduction or at least stabilisation of the malodour of the body , which is caused by enzymes; in another preferred aspect of the invention, the reduction or at least stabilisation of the enzymatic dermatitis or the rash of the skin, caused by enzymes.

It is believed that the complexing agent selectively and effectively forms a complex with the present, selected metal ions, in particular copper and iron, which are required by the enzymes for their enzymatic activity, thereby reducing or inhibiting the enzymatic activity. Thus, for example, lipolytic enzymes, which can cause lipolytic dermatitis or which can catalyse the reactions for formation of fatty acids, which cause a malodour, can be inhibited, thus preventing, reducing a malodour of the body or skin rash.

The amount of the composition of the invention used for the reduction of the enzyme activity or in the treatment, will vary with the particular location of the condition being treated, the severity of the condition being treated, the expected duration of the treatment, any specific sensitivity to either the composition specific to the user, the condition of the user, concurrent therapies being administered, other conditions present in the user.

For the present invention it is preferred that a minimum inhibitory concentration of the compositions containing the complexing agent is, preferably topically, applied to act as a complexing agent for selected metal ions present on the skin, which are required by the enzymes for their enzymatic performance, in a form such that it is available to inhibit the activity of the enzymes present, in particularly in the presence of calcium ions.

The complexing agents or compositions are in particular useful for the reduction of the enzyme activity of esterase enzymes, and thus for inhibition or inactivation of esterases, such as lipases or lipolytic enzymes. Their general activity is to hydrolyse fats present in the ester form (such as the glycerides found in human skin), and accordingly generate fatty acids and glycerol, which can cause irritation and malodour of the body. Because this group of enzymes is so widely distributed in plants, moulds, bacteria, milk, and

milk-products, as well as in almost all animal tissues, and because moreover human lipase enzymes are present in the pancreatic exudates, they are almost always present in or on the human or animal body.

The composition of the invention can be directly applied to the skin which is in contact with enzymes. Such compositions can be comprised in cosmetic composition, being in the form of a cream, lotion, foam, oil, ointment, powder or gel, which can be topically applied to the skin.

Highly preferred can be that the compositions are contained in a deodorant.

Alternatively, the compositions of the invention can be applied to an absorbent article, which can be brought in close contact with the skin which is in contact with the lipolytic enzymes. Such articles are preferably disposable articles such as diapers, incontinent pads, training pants, sanitary towels, feminine hygiene garments, dry or wet wipes.

The compositions can be prepared by any method known in the art for preparation for cosmetic compositions. The exact method will depend on the nature of the composition. The complexing agent can be added to the compositions in its acid or salt form, or be combined with other ingredients commonly used in cosmetic compositions, or dispersed or dissolved in water or oil or a water-in-oil emulsion prior to addition to the composition.

Nickel or Copper Dermatitis

The aqueous compositions of the invention can be useful in or as compositions for treatment of metal dermatitis, in particular nickel or copper dermatitis. Thus, in accord with the invention, the complexing agents described herein, can be used for preparation of aqueous compositions for treatment of metal dermatitis, in particular nickel or copper dermatitis.

The calcium ions can be comprised in the composition to be used or can be present in the composition when in use.

The preferred complexing agent herein, is EDDS, as described above.

The compositions can be prepared by any method known in the art for preparation for cosmetic compositions. The exact method will depend on the nature of the composition. The complexing agent can be added to the compositions in its acid or salt form, or be combined with other ingredients commonly used in cosmetic compositions, or dispersed or dissolved in water or oil or a water-in-oil emulsion prior to addition to the composition.

The composition can be applied directly to the skin or hair, which will be in contact with, or the vicinity of the metals or metal ions., which can be topically applied to the skin.

The compositions can also be applied (firstly) to an article, such as a wipe or tissue, which will then be applied to the skin.

The compositions of the invention can also be applied to a metal surface, which will be brought in the vicinity or contact with the skin or hair.

The required, effective amount of the composition will vary with the particular location of the condition being treated, the severity of the condition being treated, the expected duration of the treatment, any specific sensitivity to either the composition itself, or the concentration of the complexing agent to the user, the condition of the user, concurrent therapies being administered, other conditions present in the user.

The composition can comprise additional ingredients. Which ingredients are present and at which level depends on the character of the composition and the use thereof. Thus for example lotions will generally comprise different additional ingredients to powders.

It can be preferred that the compositions comprise one or more other ingredient which can reduce the metal dermatitis. Preferred can be the use of certain polymeric componds,

such as a polyoxyethylene-polyoxypropylene copolymer (Pluronic® gel), polyethylene glycols, polyurethanes, synthetic carbopol polymers, compounds which can help the healing of the skin, such as vitamins (vitamin E) and cortisone's, and also compounds to soften the skin such as vaseline, glycerin, triethyleneglycol, lanolin, paraffin and another group of polymers extensively employed by pharmaceutical and cosmetic manufactures.

The compositions can be used for any suitable purpose. In particular, the present compositions are suitable for topical application to the skin or hair. In particular, the skin care compositions can be in the form of creams, lotions, gels, and the like. Preferably the cosmetic compositions herein are in the form of an oil-in-water emulsion of one or more oil phases in an aqueous continuous phase, each oil phase comprising a single oily component or a mixture of oily components in miscible or homogeneous form but said different oil phases containing different materials or combinations of materials from each other. The overall level of oil phase components in the compositions of the invention is preferably from about 0.1% to about 60%, preferably from about 1% to about 30% and more preferably from about 1% to about 10% by weight.

Claims

1. An aqueous composition, comprising calcium ions and one or more metal ions selected from the group consisting of Cu, Fe, Zn, Ni and Co and comprising a complexing agent, whereby the $-\log_{10}C_T$ is equal to or greater than the smallest value of A or B, wherein

$$A \text{ is } -\log_{10}(L_T-M_T) \text{ and } B \text{ is } K_1(1 - K_2\sqrt{I})(1 - K_3.\exp(-K_4.P)),$$

wherein C_T is the total concentration of calcium ions, L_T is the total concentration of complexing agent, M_T is the total concentration of the metal ions, selected from the group consisting of Cu, Fe, Zn, Ni and Co; P is the pH of the composition, I is the ionic strength of the composition, whereby all concentrations are in moles/ litre, and where K1, K2, K3 and K4 are the following constants for the metals ions:

	Cu^{++}	Fe^{+++}	Zn^{++}	Ni^{++}	Co^{++}
K1	11.062	5.754	7.963	13.098	7.642
K2	0.496	0.479	0.619	0.535	0.652
K3	2.479	9385.0	24.202	1.473	32.069
K4	0.227	1.092	0.506	0.126	0.532

2. An aqueous composition according to claim 1, obtainable by a process comprising the step of addition of a complexing composition comprising a complexing agent and optional additional components to an aqueous solution comprising calcium ions.

3. An aqueous composition obtainable by a process according to claim 2, whereby the complexing composition, comprises one or more of the metal ions selected from the group consisting of Cu, Fe, Zn, Ni and Co, preferably in the form of a complex with the complexing agent.

4. An aqueous composition obtainable by a process according to claim 2 whereby the aqueous solution comprises one or more of the metal ions selected from the group consisting of Cu, Fe, Zn, Ni and Co.

5. An aqueous composition according to any preceding claim whereby the pH of the composition is at least 4 when the composition comprises copper or nickel ions, at least 7 when the composition comprises cobalt or zinc ions or at least 9.5 when the composition comprises iron ions.

6. An aqueous composition according to any preceding claim, whereby the complexing agent is an isomer of EDDS or a racemic mixture of the isomers of EDDS.

7. An aqueous composition according to any preceding claim which is not a composition for use in laundry or dish washing processes or for use in photography or photo-development processes.

8. A process according to claim 2 or 4 which is one or more steps in a reductive bleaching process.

9. A process according to claim 8 for reductive bleaching of cellulosic material, such as cotton, pulp or paper, wherein the aqueous composition comprises a sulfite-based reductive bleaching agent.

10. A process according to any of claims 2 to 4 which is one or more steps in a process for removal of metal scale.

11. A process according to any of claim 2 or 3 which is one or more steps in a process for electroless plating of metal.

12. A process according to claim 2 or 4 which is one or more steps in a fermentation process, preferably part of a process for clarification of beer or wine.

13. A process according to any of claims 2 to 4 which is one or more steps in a process for tanning of leather or human skin.

14. A process according to claim 2 or 3 which is one or more steps in a process for stabilisation or inhibition of algae, fungi or plant growth.

15. A process according to claim 2 or 4 which is one or more steps in a process for production or preservation of food.

16. Use of a complexing agent for preparation of an aqueous composition according to any of claims 1 to 7, for treatment of metal dermatitis of the external skin, preferably of copper or nickel dermatitis.

17. A process according to claims 2 or 4 which is one or more steps of a process for reduction of the enzymatic activity of enzymes in contact with the human or animal body or skin, preferably lipase enzymes present in the body extrudates.

18. Use of a complexing agent for preparation of an aqueous composition according to any of claims 1 to 7, for use in a process for reduction of the enzymatic activity of enzymes, in contact with the human or animal body, preferably lipase enzymes present in the body extrudates, preferably for treatment of enzymatic dermatitis or of malodour of the body.

19. Use of a complexing agent for preparation of an aqueous composition according to any of claims 1 to 7, for treatment of metal poisoning, preferably iron-loading.

20. Use of a complexing agent for preparation of an aqueous composition according to of claims 1 to 7, for stabilisation or inhibition or reduction of algae, fungi and/or plant growth.

21. Use of a complexing agent for complexing or chelating of one or more metal ions, selected from the group consisting of Cu, Fe, Zn, Ni and Co, in an aqueous composition whereby the $-\log_{10}C_T$ is equal to or greater than the smallest value of A or B, wherein

$$A \text{ is } -\log_{10}(L_T-M_T) \text{ and } B \text{ is } K_1(1 - K_2\sqrt{I})(1 - K_3.\exp(-K_4.P)),$$

wherein C_T is the total concentration of calcium ions, L_T is the total concentration of complexing agent, M_T is the total concentration of the metal ions, selected from the group consisting of Cu, Fe, Zn, Ni and Co; P is the pH of the composition, I is the ionic strength of the composition, whereby all concentrations are in moles/ litre, and where K1, K2, K3 and K4 are the following constants for the metals ions:

	Cu^{++}	Fe^{+++}	Zn^{++}	Ni^{++}	Co^{++}
K1	11.062	5.754	7.963	13.098	7.642
K2	0.496	0.479	0.619	0.535	0.652
K3	2.479	9385.0	24.202	1.473	32.069
K4	0.227	1.092	0.506	0.126	0.532

22. Use of a complexing agent for preparation of an aqueous composition according to of claims 1 to 7 for delivering of Cu, Fe, Zn, Ni and/or Co metal ions to the human or animal body or to plants, preferably for delivery to plants, of plant nutrients comprising one or more of the said metal ions.

INTERNATIONAL SEARCH REPORT

Ir ational Application No
PCT/IB 99/00122

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 D21C9/10 A61K31/195 C23C18/40 C14C3/00 C05D9/02
C05G3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D21C A61K C14C C05D C05G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 94 28464 A (DOW CHEMICAL CO) 8 December 1994 see page 2, line 22 - line 24 see claims; examples	1-11,14, 20-22
A	DE 196 30 278 A (BASF AG) 29 January 1998 see the whole document	1-9,21
A	WO 97 08288 A (DOW CHEMICAL CO) 6 March 1997 see page 9	1-6,14, 15,17, 18,21,22

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 May 1999	01/06/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Bernardo Noriega, F

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 99/00122

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 8111 Derwent Publications Ltd., London, GB; Class E14, AN 81-18831D XP002103125 & SU 734 194 B (AS URALS CHEM INST) , 18 May 1980 see abstract	1-4,7, 16-19, 21,22
P,A	"EFFECTIVE AND SPECIFIC CHELATION IN THE PRESENCE OF CALCIUM IONS" RESEARCH DISCLOSURE, vol. 133, no. 407, 1 March 1998, page 241 XP000773859 see the whole document	1-22

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int· ·tional Application No
PCT/IB 99/00122

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